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REGENERATION OF ACTIVATED CARBON BY FENTON AND PHOTO-FENTON OXIDATION FOR THE TREATMENT OF PHENOL WASTEWATER

C. T. MURANAKA(1,2), C. JULCOUR LEBIGUE(2), A. M. WILHELM(2), H. DELMAS(2), C. A. O. NASCIMENTO(1)

(1) Departamento de Engenharia Química, Escola Politécnica – Universidade de São Paulo USP, Cidade Universitária, São Paulo
05508-900 BRASIL
e-mail: cintiemi@gmail.com, oller@usp.br

(2) Université de Toulouse, Laboratoire de Génie Chimique UMR CNRS 5503, 5 rue Paulin Talabot, Toulouse
31106 FRANCE
e-mail: cinthiatiemi.muranaka@ensiacet.fr, carine.julcour@ensiacet.fr, annemarie.wilhelm@ensiacet.fr, henri.delmas@ensiacet.fr

Abstract.

Advanced Oxidation Processes have emerged as promising technologies for the recovery of carbons saturated with aromatic molecules, owing to their potency to degrade a wide range of organic pollutants by the generation of very reactive and non selective free hydroxyl radicals. The purpose of this work is to study the adsorption of phenol on activated carbons (ACs) and the consecutive in-situ regeneration of carbon by Fenton oxidation. Two different processes have been carried out:

- the first one is based on a complete batch system in order to investigate the influence of Fe^{2+} and H_2O_2 concentrations;
- the second one consists in a continuous fixed bed adsorption, followed by a batch circulation of the Fenton's reagent through the saturated AC bed, to examine the efficiency of the real process.

Two different activated carbons have been also studied: a both micro- and mesoporous AC (L27) and an only microporous one (S23).

In the batch reactor containing a 1 g/L phenol solution, the optimal conditions found for pollutant mineralization in the homogeneous Fenton system ($\text{Fe}^{2+} = 10 \text{ mmol/L}$, $[\text{H}_2\text{O}_2] = 1000 \text{ mmol/L}$, corresponding to 6.5 times the stoichiometric amount for complete mineralization) are not the best for AC regeneration: a continuous reduction of adsorption capacity of L27 from 100% to 23% is observed after 3 oxidations, due to the decrease of both AC weight and surface area. Higher concentration of Fe^{2+} (20 mmol/L) and lower concentration of H_2O_2 (2 times the stoichiometry) lead to a 50% recovery of the initial adsorption capacity during at least 4 consecutive cycles for L27, while about 20% or less for S23.

In the consecutive continuous adsorption/batch oxidation process, the regeneration efficiency reaches 30% to 40% for L27 after two cycles whatever the feed concentration (0.1 g/L or 1 g/L of phenol) and less than 10% for S23 (0.1 g/L of phenol).

During oxidation step, Total Organic Carbon removal is found to reach a limit, probably due to the formation of Fe^{3+} /organic acid complex, hindering Fe^{2+} regeneration. Such complexes are stable in usual Fenton conditions, but can be destroyed by UV radiation. A photo-Fenton test performed on L27 indeed shows almost complete mineralization and improved recovery of AC adsorption capacity although not complete (56% after two cycles).

Keywords. Activated carbon, regeneration, adsorption, Fenton, photo-Fenton, phenol

INTRODUCTION

Phenol and phenolic compounds are among the most prevalent chemical pollutants found in industrial wastewaters, due to their extensive use in petrochemical units, oil refineries, polymer and pharmaceutical industries.

Inhibitory effects of phenol on microbial activity have been reported for concentrations larger than 500 ppm^{1,2}. Therefore high loaded effluents require additional solutions to conventional biological treatment. Among possible techniques, adsorption on activated carbon (AC) is extensively applied, as it is most effective for removing organic compounds such as surfactants, pesticides, dyes, and aromatic molecules³.

However, after adsorption of toxic compounds, activated carbon becomes itself a hazardous waste that must be treated or disposed properly. Incineration of spent activated carbons is often used, but it has some major drawbacks: its operating costs, the destruction of the adsorbent, as well as the emission of possibly toxic compounds, such as chlorodioxines and chlorodibenzofuranes when the activated carbon is saturated with organochloro compounds⁴. Economical viability of processes using adsorption is thus directly related to their efficiency in regenerating and recycling the activated carbon.

Advanced Oxidation Processes (AOPs) have been considered a promising alternative technology for the remediation of toxic organic compounds. AOPs are characterized by the production of free radicals, mainly the hydroxyl radical ($\bullet\text{OH}$) that offers a high oxidation potential (2.8 V) and is able to oxidize a wide range of organic compounds. AOPs can be classified according to the different systems used to generate free radicals, such as: O_3/UV radiation, $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ radiation, $\text{H}_2\text{O}_2/\text{UV}$ radiation, TiO_2/UV radiation, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ radiation⁵⁻⁷ ... Those last two processes have been largely studied, known as the so-called Fenton and photo-Fenton systems, respectively.

The Fenton process is a combination of ferrous ions and hydrogen peroxide (Fenton's reagent). Those chemicals produce hydroxyl radicals according to Eq. 1⁸:



Recently Fenton oxidation has been successfully applied for the recovery of carbons exhausted with chlorinated organic compounds⁹ and methyl tert-butyl ether¹⁰. $\text{H}_2\text{O}_2/\text{UV}$ radiation has also been reported for the regeneration of activated carbon saturated with acetone and isopropyl alcohol¹¹.

In the present work, Fenton and photo-Fenton oxidations have been carried out in very mild conditions to destroy adsorbed phenol and in-situ regenerate activated carbon. The two-step process has been conducted using either a full batch system (preliminary experiments to study the influence of Fe^{2+} and H_2O_2 concentrations) or a continuous fixed bed adsorption, followed by a batch circulation of the Fenton's reagent through the spent AC bed.

MATERIALS

Ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2 ; 30%) were used as the source of hydroxyl radicals. Phenol was chosen as a model pollutant and the pH of the synthetic wastewater was adjusted by concentrated sulfuric acid (H_2SO_4). During Fenton experiments, samples of the reactant mixture were withdrawn at different reaction times and a quenching solution containing potassium iodide (KI, 0.1 mol/L), sodium sulfite (Na_2SO_3 , 0.1 mol/L) and sodium hydroxide (NaOH, 0.1 mol/L) was added to stop the reaction. All reagents were analytical grade.

Two types of activated carbon were used, in the form of 1-1.6 mm diameter particles: a both micro- and mesoporous AC (PICA L27) and an essentially microporous AC (PICA S23). The surface area and pore volume of the carbons were measured from nitrogen adsorption isotherms at 77K, using an ASAP 2010 analyzer (Micromeritics). Specific surface area was calculated from BET plot for relative pressures between 0.01 and 0.2. Thermogravimetry analysis (TGA) of the ACs was also performed under nitrogen flow from room temperature to 700°C at a heating rate of 10°C/min (Q600 SDT, TA Instrument).

APPARATUS

The experimental set-up used for Fenton experiments consisted in a 650 mL stirred Pyrex reactor, equipped with a jacket to control the temperature of the solution.

For preliminary batchwise experiments AC was kept inside the reactor in a small basket, whereas continuous adsorption was carried out in a stainless steel column (18.5 cm high and 1.5 cm internal diameter) packed with AC.

A peristaltic pump allowed the continuous feed of the phenol solution through the AC column during the adsorption step. The same pump was used to feed the column with the Fenton solution from the stirred reactor and back to it during the regeneration step (cf. Figure 1a).

For photo-Fenton tests, a 80W mercury UV lamp was used as light source. It was placed in jacketed quartz well, immersed in a borosilicate vessel. The photochemical reactor (Figure 1b) was included in the recycle loop (total liquid volume of 2 L).

a)

b)

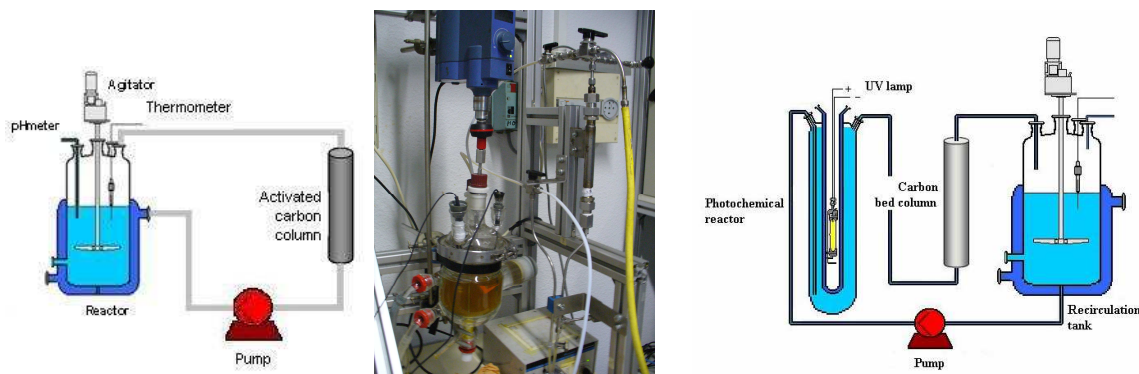


Figure 1. Fenton (a) and photo-Fenton (b) set-ups used for the regeneration of activated carbon bed.

EXPERIMENTAL PROCEDURES

Batch Adsorption System

The procedure consisted in two steps: 1) batch adsorption of phenol on activated carbon (contained in a basket); 2) Fenton oxidation. The weight of AC (S23 or L27) was calculated according to the respective adsorption isotherms so that to adsorb half of the pollutant amount initially in solution.

During the first step, 500 mL of 1 g/L phenol solution was contacted at 30°C with the activated carbon under stirring till adsorption equilibrium was reached (after 13 hours). Then, the pH of the solution was adjusted to 3.0 and the Fenton reaction was initiated by simultaneous addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and hydrogen peroxide. After the reaction step, the solution was withdrawn and another batch adsorption was carried out with a new phenol solution using the same activated carbon. This procedure was repeated 3 consecutive times with the same operating conditions. Liquid samples were taken just after adsorption and regularly during oxidation (up to 5 h). Different concentrations of Fe^{2+} (10-20 mmol/L) and H_2O_2 (300-1000 mmol/L, corresponding to 2 to 7 times the stoichiometric amount for complete mineralization) were tested for AC regeneration.

Continuous Adsorption System

In this process, a 0.1 or 1 g/L phenol solution was continuously fed to the column with a flow rate of 2 L/h till saturation of the AC bed. Then the stirred reactor was loaded with 500 mL of same phenol solution which was recycled through the bed at 2 to 6 L/h. The reactor temperature was set to 30°C and the pH adjusted to 3. The Fenton reaction was initiated by simultaneous addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and hydrogen peroxide. The oxidative regeneration step was carried out for 5 to 24 hours. Then the AC bed was drained to operate a new adsorption – oxidation cycle. Samples were regularly withdrawn at the column outlet during the two steps.

Analytical methods

After precipitation of iron using NaOH 0.1 mol/L and filtering, liquid samples were rapidly analyzed by HPLC to obtain phenol concentration. The separation was achieved by a C18 reverse phase column (ProntoSIL C18 AQ) using a mobile phase of variable composition (acidified deionised water / acetonitrile). The dual wavelength UV detector (UV2000 Thermo Finnigan) was set at 210 and 254 nm. The samples were also analyzed for remaining Total Organic Carbon (Shimadzu TOC 5050A analyzer) after addition of the quenching solution.

RESULTS AND DISCUSSION

Fenton Reaction without AC

The homogeneous Fenton reaction was first investigated for the treatment of a 1 g/L phenol solution (500 mL), varying the concentration of Fe^{2+} (from 0 to 25 mmol/L) and the amount of H_2O_2 (from 0.15 to 0.50 mol). As shown in Figure 2a, the highest mineralization was obtained for 10 mmol/L of Fe^{2+} and 0.50 mol of H_2O_2 , leading to a steady TOC conversion of 71 % after about 1 hour of reaction. In all cases, phenol was depleted within 10 to 30 minutes. The optimum found for Fe^{2+} concentration could be explained by the subsequent reaction of Fe^{2+} with the hydroxyl radicals, increasing Fe^{3+} concentration and decreasing the oxidant reagent concentration¹².

Batch Adsorption System

The optimal Fenton conditions without AC were applied for the regeneration of L27 after it had reached adsorption equilibrium with the phenol solution (exp. 1). As shown in Figure 2b, the TOC reduction obtained in liquid phase by this sequential adsorption-oxidation process was higher than that observed without AC, at least during the first cycle. However in this case the TOC vs. time plot exhibited a minimum, due to the desorption of both phenol and oxidation intermediates from AC.

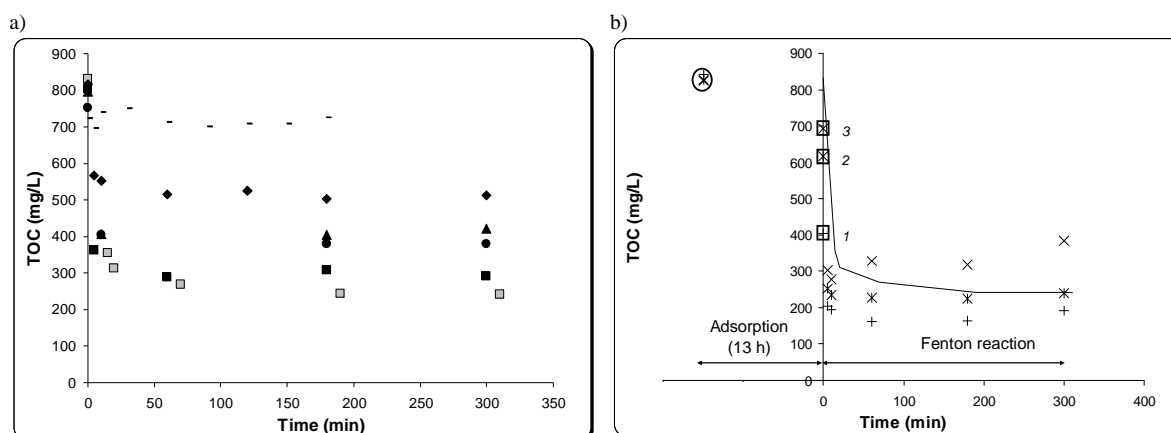


Figure 2. TOC evolution during Fenton oxidation without AC (a) and with L27 (b).

- a) $\text{H}_2\text{O}_2 = 0.50$ mol, no iron (-); $\text{H}_2\text{O}_2 = 0.50$ mol, $[\text{Fe}^{2+}] = 10$ mmol/L (\square); $\text{H}_2\text{O}_2 = 0.15$ mol, $[\text{Fe}^{2+}] = 1$ mmol/L (\blacklozenge); $\text{H}_2\text{O}_2 = 0.15$ mol, $[\text{Fe}^{2+}] = 10$ mmol/L (\blacksquare); $\text{H}_2\text{O}_2 = 0.15$ mol, $[\text{Fe}^{2+}] = 20$ mmol/L (\bullet); $\text{H}_2\text{O}_2 = 0.15$ mol, $[\text{Fe}^{2+}] = 25$ mmol/L (\blacktriangle).
- b) Exp. 1 ($\text{H}_2\text{O}_2 = 0.50$ mol, $[\text{Fe}^{2+}] = 10$ mmol/L); line: Fenton reaction without AC, dots: successive regeneration cycles [first (+), second (*) and third (x) cycle]. Empty circle and squares correspond to the beginning and end of adsorption respectively.

The regeneration efficiency was calculated as the ratio of phenol amount re-adsorbed on AC after Fenton treatment to the initial amount adsorbed, even if a more proper definition should consider values at same equilibrium aqueous phase concentration. The calculations were also based on the initial weight of AC. Corresponding results are given in Table 1. With the optimal conditions of the Fenton reaction, a continuous decrease of adsorption capacity of L27 from 100% to 23% was observed after 3 oxidations (exp. 1). It could be explained not only by some remaining physisorbed pollutants, but also by a decrease of both surface area (from 1860 to 590 m^2/g) and AC weight (from 1.7 to 1.45 g after 4 cycles). Thus a lower concentration of H_2O_2 was used to reduce AC weight loss. Iron was added in two equal parts (at $t = 0$ and $t = 60$ min) leading to a final concentration of 20 mmol/L (exp. 2). Actually a slight improvement was found when added it in once at $t = 0$ (exp. 3). The results of experiment 3 showed that the efficiency of phenol adsorption remained then practically constant at 50% for at least 4 adsorption-oxidation cycles. No AC weight loss was observed and the surface area only decreased to 1020 m^2/g in this case.

When such Fenton oxidation was applied to S23, the recovery of its adsorption capacity was found significantly lower and always decreasing. It was probably due to S23 microporous character, access to the micropores being partially blocked by condensation products resulting in a surface area divided by a factor 6 (from 1230 to 210 m^2/g). Deposit of such low-volatile compounds was put into evidence by comparing the TGA spectra of fresh and spent ACs: the weight loss between 200 and 700°C increased from 17% to 27% for L27 and from 4% to 11% for S23.

Table 1. Regeneration efficiency of L27 and S23 after Fenton treatment (batch adsorption)

Exp.	AC	m_{AC} (g)	$[\text{Fe}^{2+}]$ (mmol/L)	H_2O_2 (mol)	Regeneration efficiency (%)			
					2 nd cycle	3 rd cycle	4 th cycle	5 th cycle
1	L27	1.70	10	0.50	52.3	43.0	22.8	
2	L27	1.70	20*	0.15	40.3	52.7	43.6	37.0
3	L27	1.70	20	0.15	51.9	46.6	50.7	44.9
4	S23	0.87	20	0.15	30.6	24.8	22.1	16.6

*added in two equal parts at $t = 0$ and $t = 60$ min

The modification of the chemical surface properties of the ACs by the Fenton's reagent could also be a reason for the lower adsorption observed after regeneration; blank tests (without pollutant) showed that this phenomenon contributed for 5 to 25% of the total capacity loss for L27 carbon (conditions of exp. 3 and 1 respectively).

Continuous Adsorption System

To mimic a real process, a continuous adsorption was achieved prior to the in-situ regeneration. However the adsorption step was carried on up to complete AC saturation, so that the adsorption capacity of (fresh/regenerated) ACs could be calculated from numerical integration of the breakthrough curves (cf. Figure 3a). According to the previous results, the amount of H₂O₂ added for the regeneration corresponded to about 2 times the stoichiometry for complete mineralization of phenol - adsorbed and in solution (exp. 1-3). Results are shown in Table 2.

Table 2. Regeneration efficiency of L27 and S23 after Fenton treatment (continuous adsorption)

Exp	AC	m _{AC} (g)	Phenol feed (g/L)	[Fe ²⁺] (mmol/L)	H ₂ O ₂ (mol)	Regeneration efficiency (%)			S _{BET} decrease (%)
						2 nd cycle	3 rd cycle	4 th cycle	
1	S23	6.0	0.1	20 ^a -40 ^b	0.25 ^a -0.35 ^b	11.8	7.8	-	60.0
2	L27	9.8	0.1	20	0.25	37.7	29.5	29.9	39.6
3	L27	9.8	1.0	20	0.74 ^c	47.3	31.2	-	71.3
4 ^d	L27	8.4	1.0	2	0.62 ^e	49.4	40.5	-	48.3

t_{oxidation} = 5 h with Q_{recirculation} = 6 L/h if not mentioned otherwise

^a 1st cycle (t_{oxidation} = 24 h, Q_{recirculation} = 2 L/h); ^b 2nd cycle (Q_{recirculation} = 2 L/h); ^c added in four equal parts; ^d liquid volume = 2 L; ^e added in four equal parts and equivalent to 1.1 time the stoichiometry for complete mineralization (Q_{recirculation} = 2 L/h)

In accordance with previous batch observations, the Fenton treatment was much more efficient for L27 than for S23. An interesting result is that the recovery yield appeared to be almost independent of the feed concentration used in adsorption (0.1 or 1 g/L), despite the decrease of S_{BET} was higher when increasing the adsorbed pollutant amount.

Photo-Fenton regeneration

During the Fenton oxidation, mineralization yield reached its maximum after one hour and never decayed afterwards (cf. Figures 2a and b). Such reaction inhibition could be explained by the formation of Fe³⁺/carboxylic acids complexes (Eq. 2), hindering the Fe²⁺ regeneration^{13,14}:



Those complexes are stable in usual Fenton conditions, but can be destroyed by UV radiation according to the following reaction:



UV light can also enhance mineralization by the photoreduction of Fe³⁺ to Fe²⁺ (Eq. 4), accelerating Fe²⁺ regeneration and generating additional hydroxyl radicals.



The effect of UV radiation was investigated for the conditions of exp. 4. During the oxidation step, 95% mineralization was achieved in solution after 4 hours with photo-Fenton, while only 25% with Fenton.

Figures 3a and b compare the corresponding adsorption curves after Fenton and photo-Fenton treatments. Although the adsorption capacity of L27 decreased upon recycling in both cases, it could be maintained to 56% of its original capacity after two cycles with photo-Fenton oxidation (against 40% with “dark” Fenton). The change in BET surface area appeared to be the same after both treatments.

a)

b)

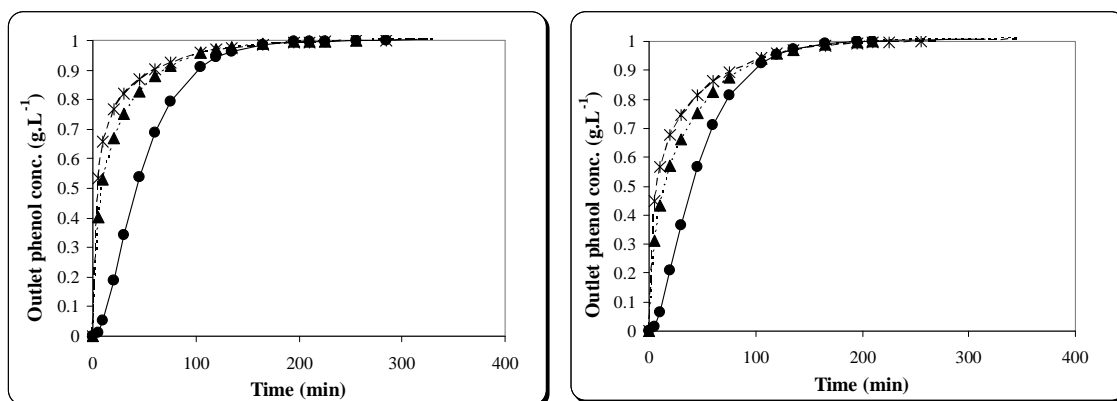


Figure 3. Successive breakthrough curves of phenol with L27 carbon after Fenton (a) and photo-Fenton (b) regeneration (adsorption step: flow rate = 2 L/h, solution feed = 1 g/L; oxidation step: conditions of exp. 4): fresh AC (●), AC after first (▲) and second (*) adsorption-oxidation cycle.

CONCLUSIONS

The experimental results presented in this work showed that Fenton and photo-Fenton processes are applicable to regenerate spent activated carbons saturated with phenol.

The regeneration efficiency was found to be a complex interplay between the mineralization yield and the modification of both textural and chemical surface properties of the activated carbons.

Concerning Fenton treatment, a lower recovery of phenol adsorption capacity was obtained for the microporous AC (S23) than for the both meso- and micro-porous AC (L27), whatever the system considered (spent AC immersed in the Fenton solution or circulation of the reagent through the saturated AC bed). It may be explained by a significant decrease of S23 specific area after the oxidation steps, even if in case of L27 similar performances could be obtained for different aging of the AC.

It was also found that UV irradiation improved the mineralization yield and the subsequent re-adsorption (by more than 15% compared to “dark” Fenton treatment).

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